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(21)	(A1)	2,137,540
(22)		1994/12/07
(43)		1995/06/10

(51) Int.Cl. <sup>5</sup> C07C 271/28; C08G 18/79; C08G 18/10; C08L 75/04

(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Preparation of Compact or Cellular Polyurethanes,  
Polyisocyanate Compositions Containing Urethane Groups  
Which Can Be Used for This Purpose, and Their Use

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(30) (DE) P 43 41 973.0 1993/12/09

(57) 10 Claims

Notice: This application is as filed and may therefor contain an  
incomplete specification.



Preparation of compact or cellular polyurethanes, polyisocyanate compositions containing urethane groups which can be used for this purpose, and their use

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## Abstract

The invention relates to a process for the preparation of compact or cellular polyurethanes by reacting relatively high-molecular-weight polyhydroxyl compounds with a liquid polyisocyanate composition containing urethane groups in the presence or absence of chain extenders and/or crosslinking agents, the polyisocyanate composition being obtainable from mixtures of diphenylmethane diisocyanates and polyphenylpolymethylene polyisocyanates and linear, branched or cyclic, saturated or olefinically unsaturated, low-molecular-weight monoalcohols, to the liquid polyisocyanate compositions containing urethane groups which can be used for this purpose, and to their use for the preparation of preferably highly crosslinked polyurethanes, in particular rigid PU (molded) foams.

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Preparation of compact or cellular polyurethanes, polyisocyanate compositions containing urethane groups which can be used for this purpose, and their use

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The invention relates to a process for the preparation of compact or preferably cellular polyurethanes, in particular rigid polyurethane (PU) foams, by reacting relatively high-molecular-weight polyhydroxyl compounds (a) with a liquid polyisocyanate composition (b) containing bonded urethane groups in the presence or  
10 absence of chain extenders and/or crosslinking agents (c), where this polyisocyanate composition (b) is itself obtainable by reacting a mixture of diphenylmethane diisocyanates (MDI) and polyphenylpolymethylene polyisocyanates, known as crude MDI, and  
15 linear, branched or cyclic, saturated or olefinically unsaturated, low-molecular-weight monoalcohols, expediently having 1 to 6 carbon atoms, to novel polyisocyanate compositions (b) of this type, and to their use for the preparation of preferably highly crosslinked polyurethanes, in particular rigid polyurethane  
20 foams.

The preparation of compact or cellular polyurethanes, also abbreviated to PU below, preferably soft and elastic, semirigid or rigid polyurethane foams, by reacting relatively high-molecular-weight polyhydroxyl compounds, preferably polyester- or in  
25 particular polyether-polyols, with organic and/or modified organic polyisocyanates in the presence or absence of chain extenders and/or crosslinking agents is known and is described in numerous patents and other publications.

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By way of example, reference may be made to Kunststoff-Handbuch, Volume VII, Polyurethanes, Carl Hanser Verlag, Munich, Vienna, 1st Edition, 1966, edited by Dr. R. Vieweg and Dr. A. Höchtlen, and 2nd Edition, 1983, edited by Dr. G. Oertel.

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Compact and cellular polyurethanes are usually prepared by the two-component process, in which a component A containing the relatively high-molecular-weight polyhydroxyl compounds, if desired chain extenders, crosslinking agents, blowing agents, catalysts,  
40 auxiliaries and/or additives, and component B, which usually comprises organic and/or modified organic polyisocyanates, are mixed vigorously and brought to reaction. Although the two-component process is widely used in industry, it still has deficiencies. For example, an evident problem is the poor compatibility of the  
45 polyhydroxyl component (A) and the polyisocyanate component (B), which occurs, in particular, in the reaction of highly functional polyether-polyols based on at least trifunctional initiator

molecules, for example glycerol, trimethylolpropane, pentaerythritol, sorbitol and sucrose, with crude MDI having a functionality of greater than 2.5. This therefore requires longer stirring times before compatibility of the starting components is achieved owing to commencement of urethane formation or special mixing techniques, by means of which the sometimes coarse dispersions of one starting component in the other can be converted into fine emulsions. The polyurethane formation thus takes place at the beginning of a reaction from 2 heterogeneous phases to a certain conversion, presumably due to the oligomers which become effective solubilizers, from which fine emulsions and/or true solutions are formed. This phase change is evident, for example, from the conversion of the yellow-brown, cloudy dispersions or emulsions into a dark-brown, clear solution.

There is thus a close relationship between the quality of the compact or cellular polyurethanes formed and the starting materials used, their physical and chemical properties, the mixing technique used and the reaction mixture obtained, which can be in the form, for example, of a coarse dispersion, fine emulsion or clear solution, or anywhere in between.

There has therefore been no lack of attempts to improve the mechanical properties of polyurethanes by a suitable choice of starting materials or by modification thereof in order largely to overcome the abovementioned disadvantages.

Reference may be made, for example, to processes for the liquefaction of MDI isomer mixtures or processes for improving the low-temperature shelf life of crude MDI, in particular crude MDI having a relatively high content of MDI isomers, by partial reaction of the polyisocyanates with polyhydric alcohols.

According to DE-C-16 18 380 (US-A-3,644,457), this is achieved by reacting 1 mol of 4,4'- and/or 2,4'-MDI with from 0.1 to 0.3 mol of tri-1,2-oxypropylene glycol and/or poly-1,2-oxypropylene glycol having a molecular weight of up to 700.

According to GB-A-1,369,334, the modification is carried out in two reaction steps and the modifier used is dipropylene glycol or polyoxypropylene glycol having a molecular weight of less than 2000.

DE-A-29 13 126 (US-A-4,229,347) describes MDI compositions in which from 10 to 35% by weight of the isocyanate groups are reacted with a mixture of at least 3 alkylene glycols, one of

these glycols being di-, tri- or a relatively high-molecular-weight polyoxypropylene glycol.

By contrast, the modifiers used in DE-A-24 04 166

- 5 (GB-A-1,430,455) are mixtures of a polyoxyethylene glycol or polyoxyethylene glycol mixture having a mean molecular weight of less than 650 and at least one alkylene glycol containing at least 3 carbon atoms.
- 10 DE-A-23 46 996 (GB-A-1,377,679) relates to MDI compositions in which from 10 to 35% by weight of the isocyanate groups have been reacted with a commercially available polyoxyethylene glycol..
- EP-A-10 850 uses a crude MDI composition comprising a mixture of 15 crude MDI with an MDI which has been modified by means of polyoxyalkylene polyols having a functionality of from 2 to 3 based on polyoxypropylene-polyol and, if desired, polyoxyethylene-polyol having a molecular weight of from 750 to 3000.
- 20 According to DE-B-27 37 338 (UA-A-4,055,548), a liquid crude MDI composition is obtained by combining crude MDI with a polyoxyethylene glycol having a mean molecular weight of from 200 to 600.
- 25 In DE-B-26 24 526 (GB-A-1,550,325), a crude MDI which has been prepared by a special process and contains from 88 to 95% by weight of MDI is reacted with polyoxypropylene glycol having a molecular weight in the range from 134 to 700.
- 30 DE-A-25 13 796 (GB-A-1,444,192) and DE-A-25 13 793 (GB-A-1,450,660) relate to crude MDI compositions in which the crude MDI has been modified by means of alkylene glycols or polyoxyalkylene glycols in certain amounts.
- 35 Although said alkylene glycols or polyoxyalkylene glycols cause liquefaction of the 4,4'- or 2,4'-MDI isomers, which melt at 42° and 28°C respectively, it is disadvantageous that the polyisocyanate compositions exhibit crystalline deposits after extended storage at temperatures around 10°C.
- 40  
It is furthermore known that flexible PU foams can be produced using, as the polyisocyanate component, crude MDI compositions which have been modified by means of urethane groups.
- 45 In EP-A-22 617, this is achieved by reacting a difunctional to trifunctional polyoxypropylene-polyoxyethylene-polyol containing at least 50% by weight of the polymerized oxyethylene groups with

a mixture of MDI isomers and subsequently diluting the resultant quasi-polymer with crude MDI. A particular disadvantage of the PU foams described is their low tensile strength and tear propagation strength.

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Polyisocyanate mixtures based on crude MDI which have been modified by means of urethane groups and contain from 12 to 30% by weight of NCO groups are also described in EP-B-0 111 121 (US-A-4,478,960). The MDI or crude MDI is modified using a polyoxypropylene-polyoxyethylene-polyol having a functionality of  
 10 from 2 to 4, a hydroxyl number of from 10 to 65 and a content of polymerized ethylene oxide units of from 5 to 30% by weight. Using these polyisocyanate mixtures which have been modified by means of urethane groups, PU foams having increased elongation at  
 15 break, improved tensile strength and tear propagation strength can be produced.

However, the modification of the MDI isomer mixtures and relatively highly functional crude MDI by means of low-molecular-weight alkanediols and/or oxyalkylene glycols and/or relatively  
 20 high-molecular-weight, at least difunctional polyoxyalkylene-polyols is severely restricted, since even partial reaction of these starting materials causes a very considerable increase in the functionality and thus in the viscosity of the resultant  
 25 polyisocyanate compositions which have been modified by means of urethane groups. The high viscosities of crude MDI compositions of this type mean that they can only be processed with difficulty in conventional metering and foaming equipment.

EP-A-0 320 134 states that the compatibility of the polyhydroxyl component (A) and the polyisocyanate component (B) can be improved by using polyisocyanate compositions having a functionality of at least 2.3 which comprise, based on the total weight, from 30 to 45% by weight of MDI, from 28 to 67% by weight of  
 30 polyphenylpolymethylene polyisocyanates containing more than 2 isocyanate groups and from 3 to 27% by weight of a prepolymer prepared from MDI and a compound containing at least 2 radicals which react with isocyanate groups and having a molecular weight of less than 1000. Disadvantages of these MDI compositions are  
 40 their two-step preparation method and, as a consequence of the increase in viscosity, the fact that compounds containing at least 2 radicals which react with isocyanate groups can only be used in limited amounts.

45 In order to overcome these disadvantages, DE-A-39 28 330 (US-A-5,028,636) reacts MDI or crude MDI having an MDI content of at least 30% by weight with substoichiometric amounts of at least

one alkoxylation product obtained using monoalcohols having 8 to 24 carbon atoms, primary amines or organic carboxylic acids as initiator molecules. EP-A-031 650 describes the modification of MDI mixtures containing at least 15% by weight of 2,4'-MDI by means of a monohydric alcohol having 9 to 16 carbon atoms or a polyoxyalkylene alcohol containing 1 to 58 alkylene oxide groups and an alkyl terminal group having 1 to 12 carbon atoms. Through incorporation of the relatively high-molecular-weight alkyl radicals or polyoxyalkylene groups into the crude MDI or MDI, the adducts obtained are said to be effective in the form of an "internal" emulsifier and to improve the miscibility of polyoxyalkylene-polyols and crude MDI compositions. However, these measures do not adequately solve the main problem of incompatibility or immiscibility of highly functional, hydrophilic polyhydroxyl compounds, in particular polyoxyalkylene-polyols, and hydrophobic polyisocyanates, in particular crude MDI.

It is an object of the present invention to improve the mechanical properties of compact and cellular polyurethanes, preferably rigid PU foams. To this end, it is an object to use measures which can readily be carried out industrially to improve the miscibility of the starting materials, preferably the miscibility of the polyhydroxyl component (A) and the polyisocyanate component (B).

We have found that, surprisingly, this object is achieved by increasing the content of urethane groups in the polyisocyanate composition, which allows the compatibility of polyisocyanate compositions based on MDI with polyhydroxyl compounds, preferably polyether-polyols, to be improved, so that, for example, directly after components (A) and (B) have been mixed, true solutions or fine emulsions are formed.

The present invention accordingly provides a process for the preparation of compact or preferably cellular polyurethanes, in particular rigid polyurethane foams, by reacting

- a) relatively high-molecular-weight polyhydroxyl compounds containing at least two reactive hydrogen atoms with
  - b) liquid, diphenylmethane diisocyanate-based polyisocyanate compositions containing bonded urethane groups,
- in the presence or absence of
- c) chain extenders and/or crosslinking agents,



- d) blowing agents,
- e) catalysts and
- 5 f) auxiliaries,

wherein the polyisocyanate compositions (b) used are obtainable by reacting mixtures of diphenylmethane diisocyanates and polyphenylpolymethylene polyisocyanates with a substoichiometric  
10 amount of at least one linear, branched or cyclic, saturated or olefinically unsaturated, low-molecular-weight monoalcohol.

The present invention furthermore provides the liquid polyisocyanate compositions containing urethane groups which can be used  
15 according to the invention, which are obtainable by reacting mixtures of diphenylmethane diisocyanates and polyphenylpolymethylene polyisocyanates with a substoichiometric amount of at least one linear, branched or cyclic, saturated or olefinically unsaturated, low-molecular-weight monoalcohol having 1 to 6 carbon  
20 atoms as claimed in claim 6, and the use of these liquid polyisocyanate compositions containing urethane groups for the production of, in particular, rigid polyurethane foams as claimed in claim 10.

25 Partial reaction of crude MDI with the low-molecular-weight, monohydric alcohols allows the urethane group content, which is advantageously greater than or equal to 0.1 mol/kg of polyisocyanate composition, to be increased as desired in accordance with requirements, for example its compatibility depending on the type  
30 of polyhydroxyl component (A), without any excessive increase in the viscosity of the polyisocyanate composition (b) and thus without making its processibility more difficult or even impossible. When the monohydric alcohols suitable according to the invention are used to form the urethane groups, crude MDI compositions having a content of urethane groups of, for example,  
35 0.4 mol/kg are of low viscosity and preferably give clear solutions on mixing with the polyhydroxyl component (A), while crude MDI compositions having the same urethane group content, but prepared using dihydric and/or trihydric alcohols are no longer processible in conventional foaming equipment due to their high  
40 viscosity.

Reaction of the crude MDI with the monohydric alcohols reduces the functionality of the polyisocyanate composition (b), but,  
45 surprisingly, this measure has virtually no adverse effect on the mechanical properties of the resultant compact or cellular polyurethanes, in particular rigid PU foams. The crucial factor for

this may well be that fine emulsions are rapidly converted into homogeneous solutions, or homogeneous solutions directly, which readily give reproducible polyurethanes of constant quality already obtained at the beginning of the mixing operation from the crude MDI compositions containing urethane groups and modified according to the invention and the polyhydroxyl component (A), irrespective of the mixing quality of the mixing device. In the case of rigid PU foams, it is not only the mechanical properties in general terms, but in particular its compressive strength that has been improved by means of the process according to the invention.

It is furthermore advantageous that the maximum reaction temperature which occurs during the preparation of the rigid PU foam can be significantly reduced, so that discoloration or tarring of the core of the rigid PU foam is prevented.

The following details apply to the novel process for the preparation of the compact or preferably cellular polyurethanes, in particular rigid PU foams, and to the starting materials which can be used for this purpose:

- a) Suitable relatively high-molecular-weight polyhydroxyl compounds (a) usually have a functionality of from 2 to 8 and a molecular weight of from 400 to 8000, the flexible polyurethanes expediently being prepared using polyhydroxyl compounds having a functionality of, preferably, from 2 to 3 and a molecular weight of, preferably, from 2400 to 7200, in particular from 3200 to 6000, and rigid polyurethanes expediently being prepared using polyhydroxyl compounds having a functionality of, preferably, from 3 to 8, in particular from 3 to 6, and a molecular weight of, preferably, from 400 to 3600, in particular from 1200 to 3200. Preferred polyhydroxyl compounds are linear and/or branched polyester-polyols, in particular polyoxyalkylene-polyols. However, polymer-modified polyoxyalkylene-polyols, polyoxyalkylene-polyol dispersions and other hydroxyl-containing polymers and polycondensates having the abovementioned functionalities and molecular weights, for example polyester-amides, polyacetals and/or polycarbonates, in particular those prepared from diphenyl carbonate and 1,6-hexanediol by transesterification, or mixtures of at least two of said relatively high-molecular-weight polyhydroxyl compounds, are also suitable.
- Suitable polyester-polyols may be prepared, for example, from organic dicarboxylic acids having from 2 to 12 carbon atoms, preferably aliphatic dicarboxylic acids having from 4 to

6 carbon atoms and polyhydric alcohols, preferably alkanediols, having from 2 to 12 carbon atoms, preferably from 2 to 6 carbon atoms and/or dialkylene glycols. Examples of suitable dicarboxylic acids are succinic acid, glutaric acid, adipic acid, suberic acid, azelaic acid, sebacic acid, decanedicarboxylic acid, maleic acid, fumaric acid, phthalic acid, isophthalic acid and terephthalic acid. The dicarboxylic acids may be used either individually or mixed with one another. The free dicarboxylic acids may also be replaced by the corresponding dicarboxylic acid derivatives, for example dicarboxylic esters of alcohols having 1 to 4 carbon atoms or dicarboxylic anhydrides. Preference is given to dicarboxylic acid mixtures comprising succinic acid, glutaric acid and adipic acid in ratios of, for example, from 20 to 35: 35 to 50: 20 to 32 parts by weight, and in particular adipic acid. Examples of dihydric and polyhydric alcohols, in particular alkanediols and dialkylene glycols, are ethanediol, diethylene glycol, 1,2- and 1,3-propanediol, dipropylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,10-decanediol, glycerol and trimethylolpropane. Preference is given to ethanediol, diethylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol and mixtures of at least two of said alkanediols, in particular mixtures of 1,4-butanediol, 1,5-pentanediol and 1,6-hexanediol. Furthermore, polyester-polyols made from lactones, eg.  $\epsilon$ -caprolactone or hydroxycarboxylic acids, eg.  $\omega$ -hydroxycaproic acid, may also be employed.

The polyester-polyols may be prepared by polycondensing the organic, eg. aromatic and preferably aliphatic polycarboxylic acids and/or derivatives thereof and polyhydric alcohols and/or alkylene glycols without using a catalyst or preferably in the presence of an esterification catalyst, expediently in an inert gas atmosphere, eg. nitrogen, helium, argon, inter alia, in the melt at from 150 to 250°C, preferably from 180 to 220°C, at atmospheric pressure or under reduced pressure until the desired acid number, which is advantageously less than 10, preferably less than 2, is reached. In a preferred embodiment, the esterification mixture is polycondensed at the abovementioned temperature under atmospheric pressure and subsequently under a pressure of less than 500 mbar, preferably from 50 to 150 mbar, until an acid number of from 80 to 30, preferably from 40 to 30, has been reached. Examples of suitable esterification catalysts are iron, cadmium, cobalt, lead, zinc, antimony, magnesium, titanium and tin catalysts in the form of metals, metal oxides or metal salts. However, the polycondensation may also be

carried out in the liquid phase in the presence of diluents and/or entrainers, eg. benzene, toluene, xylen or chlorobenzene, for removal of the water of condensation by azeotropic distillation.

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The polyester-polyols are advantageously prepared by polycondensing the organic polycarboxylic acids and/or derivatives thereof with polyhydric alcohols in a molar ratio of from 1:1 to 1.8, preferably from 1:1.05 to 1.2.

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The polyester-polyols obtained preferably have a functionality of from 2 to 4, in particular from 2 to 3, and a molecular weight of from 800 to 3600, preferably from 1200 to 3200, in particular from 1800 to 2500.

15

However, the preferred polyhydroxyl compounds are polyoxyalkylene-polyols prepared by conventional processes, for example by anionic polymerization using alkali metal hydroxides such as sodium hydroxide or potassium hydroxide, or alkali metal alkoxides, such as sodium methoxide, sodium ethoxide, potassium ethoxide or potassium isopropoxide as catalysts and with addition of at least one initiator molecule containing from 2 to 8, preferably 2 or 3, reactive hydrogen atoms in bound form for the preparation of polyoxyalkylene-polyols for flexible polyurethanes and preferably from 3 to 8 reactive hydrogen atoms in bound form for the preparation of polyoxyalkylene-polyols for semirigid and rigid polyurethanes, or by cationic polymerization using Lewis acids, such as antimony pentachloride, boron fluoride etherate, inter alia, or bleaching earth as catalysts, from one or more alkylene oxides having from 2 to 4 carbon atoms in the alkylene moiety.

Examples of suitable alkylene oxides are tetrahydrofuran, 1,3-propylene oxide, 1,2- and 2,3-butylene oxide and preferably ethylene oxide and 1,2-propylene oxide. The alkylene oxides may be used individually, alternatively one after the other or as mixtures. Examples of suitable initiator molecules are water, organic dicarboxylic acids, such as succinic acid, adipic acid, phthalic acid and terephthalic acid, aliphatic and aromatic, unsubstituted or N-mono-, N,N- and N,N'-dialkyl-substituted diamines having from 1 to 4 carbon atoms in the alkyl moiety, such as unsubstituted or mono- or dialkyl-substituted thyl n diamine, diethylenetriamine, triethylenetetramine, 1,3-propylenediamine, 1,3- and 1,4-butylenediamine, 1,2-, 1,3-, 1,4-, 1,5- and 1,6-hexamethylen diamine, phenyl n diamines, 2,3-, 2,4- and

2,6-tolylenediamine and 4,4'-, 2,4'- and 2,2'-diaminodiphenylmethane.

5 Other suitable initiator molecules are alkanolamines, eg. ethanolamine, N-methyl- and N-ethyl-ethanolamine, dialkanolamines, eg. diethanolamine, N-methyl- and N-ethyl-diethanolamine, and trialkanolamines, eg. triethanolamine, and ammonia. Preference is given to polyhydric alcohols, in particular dihydric to octahydric alcohols and/or alkylene glycols, eg. ethanediol, 1,2- and 1,3-propanediol, diethylene glycol, dipropylene glycol, 1,4-butanediol, 1,6-hexanediol, glycerol, trimethylolpropane, pentaerythritol, sorbitol and sucrose or mixtures of at least two polyhydric alcohols.

15 The polyoxyalkylene-polyols, preferably polyoxypropylene- and polyoxypropylene-polyoxyethylene-polyols, have a functionality of from 2 to 8 and molecular weights of from 400 to 8000, where, as stated above, polyoxyalkylene-polyols having a functionality of from 2 to 3 and a molecular weight of from 2400 to 7200 are preferred for flexible polyurethanes and 20 polyoxyalkylene-polyols having a functionality of from 3 to 8 and a molecular weight of from 400 to 3600 are preferred for rigid polyurethanes, and suitable polyoxytetramethylene glycols have a molecular weight of from 400 to approximately 3500.

Other suitable polyoxyalkylene-polyols are polymer-modified polyoxyalkylene-polyols, preferably graft polyoxyalkylene-polyols, in particular those based on styrene and/or acrylonitrile and prepared by in situ polymerization of acrylonitrile, styrene or preferably mixtures of styrene and acrylonitrile, for example in a weight ratio of from 90:10 to 10:90, preferably from 70:30 to 30:70, expediently in the abovementioned polyoxyalkylene-polyols by a method similar to 35 that of German Patents 11 11 394, 12 22 669 (US 3,304,273, 3,383,351 and 3,523,093), 11 52 536 (GB 1,040,452) and 11 52 537 (GB 987,618), and polyoxyalkylene-polyol dispersions which contain, as the disperse phase, usually in an amount of from 1 to 50% by weight, preferably from 2 to 25% 40 by weight, for example polyureas, polyhydrazides, polyurethanes containing tert-amino groups in bound form, and/or melamine and are described, for example, in EP-B-011 752 (US 4,304,708), US-A-4,374,209 and DE-A-32 31 497.

45 Lik the polyester-polyols, the polyoxyalkylene-polyols can be used individually or in the form of mixtures. Furthermore, they may be mixed with the graft polyoxyalkylene-polyols or

polyester-polyols and the hydroxyl-containing polyester-amides, polyacetals and/or polycarbonates. Examples of mixtures which have proven highly suitable for flexible polyurethanes are those having a functionality of from 2 to 3 and a molecular weight of from 2400 to 8000 which contain at least one polyoxyalkylene-polyol and at least one polymer-modified polyoxyalkylene-polyol from the group consisting of graft polyoxyalkylene-polyols or polyoxyalkylene-polyol dispersions containing, as disperse phase, polyureas, polyhydrazides or polyurethanes containing bonded tertiary amino groups.

Examples of suitable hydroxyl-containing polyacetals are the compounds which can be prepared from glycols, such as diethylene glycol, triethylene glycol, 4,4'-dihydroxyethoxydiphenyldimethylmethane, hexanediol and formaldehyde. Suitable polyacetals can also be prepared by polymerizing cyclic acetals.

Suitable hydroxyl-containing polycarbonates are those of a conventional type, which can be prepared, for example, by reacting diols, such as 1,3-propanediol, 1,4-butanediol and/or 1,6-hexanediol, diethylene glycol, triethylene glycol or tetraethylene glycol, with diaryl carbonates, eg. diphenyl carbonate, or phosgene.

The polyester-amides include, for example, the predominantly linear condensates obtained from polybasic, saturated and/or unsaturated carboxylic acids or anhydrides thereof and polyhydric, saturated and/or unsaturated amino alcohols, or mixtures of polyhydric alcohols and amino alcohols and/or polyamines.

b) The organic polyisocyanates used according to the invention are liquid, diphenylmethane diisocyanate-based polyisocyanate compositions (b) containing urethane groups which are obtainable by reacting mixtures of diphenylmethane diisocyanates (MDI) and polyphenylpolymethylene polyisocyanates, usually known as crude MDI, with a substoichiometric amount of at least one linear, branched or cyclic, saturated or olefinically unsaturated, low-molecular-weight monoalcohol.

Suitable crude MDI grades advantageously have, in addition to higher homologs, a content of MDI isomers of from 30 to 95% by weight, preferably from 35 to 80% by weight, based on the total weight, and NCO contents of from approximately 30 to

32% by weight. Highly suitable are crude MDIs which contain or preferably comprise, based on the total weight:

5        bI<sub>1</sub>) from 29 to 65% by weight, preferably from 33 to 60% by weight, of 4,4'-MDI,

bI<sub>2</sub>) from 1 to 30% by weight, preferably from 2 to 20% by weight, of 2,4'-MDI,

10       bI<sub>3</sub>) from 0 to 4% by weight, preferably from 0.5 to 2.5% by weight, of 2,2'-MDI and

15       bI<sub>4</sub>) from 70 to 5% by weight, preferably from 65 to 20% by weight, of at least trifunctional polyphenylpolymethylene polyisocyanates.

20       For the purposes of the present invention, liquid polyisocyanate compositions containing urethane groups which can be used according to the invention are also taken to mean polyisocyanate compositions obtained by reacting mixtures of MDI isomers with the low-molecular-weight monoalcohols and subsequently blending the resultant MDI mixtures containing urethane groups with the abovementioned crude MDI and/or the crude MDI compositions containing urethane groups prepared according to the invention or by blending the crude MDI compositions containing urethane groups prepared according to the invention with MDI mixtures and/or MDI mixtures containing urethane groups.

30       Suitable mixtures of MDI isomers expediently contain or preferably comprise, based on the total weight

35       bII<sub>1</sub>) from 90 to 48% by weight, preferably from 80 to 60% by weight, of 4,4'-MDI,

bII<sub>2</sub>) from 10 to 48% by weight, preferably from 20 to 40% by weight, of 2,4'-MDI and

40       bII<sub>3</sub>) from 0 to 4% by weight, preferably from 0 to 2.5% by weight, of 2,2'-MDI.

45       Preferred low-molecular-weight monoalcohols for the preparation of the liquid diphenylmethane diisocyanate-based polyisocyanate compositions (b) containing bonded urethane groups are those having 1 to 6 carbon atoms, in particular 1 to 3 carbon atoms, from the group consisting of linear or branched, saturated, monohydric alcohols. It is also possible

to use linear or branched, olefinically unsaturated, monohydric alcohols having 3 to 6 carbon atoms and saturated or olefinically unsaturated, cyclic, monohydric alcohols having 4 to 6 carbon atoms, preferably 5 or 6 carbon atoms. Specific  
5 mention may be made, by way of example, of the following: linear and branched, saturated monoalcohols, eg. methanol, ethanol, n-propanol, isopropanol, n-butanol, n-pentanol and n-hexanol and the corresponding structurally isomeric monohydric alcohols, linear and branched, olefinically unsaturated  
10 monoalcohols, eg. allyl alcohol, 2-methyl-2-propen-1-ol, 2- and 3-buten-1-ol, and cyclic, saturated or olefinically unsaturated monoalcohols, eg. cyclobutanol, cyclopentanol, cyclopentenol, cyclohexanol and cyclohexenol. Monoalcohols which have proven highly successful and are therefore preferred  
15 are methanol, ethanol, n-propanol, isopropanol and allyl alcohol. The low-molecular-weight monoalcohols can be employed in technical-grade or preferably pure form, individually or as mixtures of at least two monoalcohols.

20 As mentioned above, the compatibility of the polyhydroxyl component (A) and the polyisocyanate component (B) depends on the type of the polyhydroxyl component (A) and the content of urethane groups in the polyisocyanate component (B), which is expediently at least 0.1 mol, preferably from 0.1 to 2 mol,  
25 in particular from 0.4 to 1 mol, of urethane groups per kg of polyisocyanate composition. If the polyisocyanate composition has a urethane group content of from 0.1 to 0.3 mol/kg, a fine emulsion which is very rapidly converted into a clear, homogeneous mixture is in some cases initially formed on mixing  
30 the polyhydroxyl component (A) and the polyisocyanate component (B), depending on the type of the polyhydroxyl component (A), while polyisocyanate compositions have a urethane group content of approximately 0.4 mol/kg or greater usually form clear solutions directly on mixing. The polyisocyanate  
35 compositions containing urethane groups which have been modified according to the invention by means of monohydric alcohols usually have, in the range from 0.4 to 1 mol of urethane groups/kg, a viscosity, measured at 23°C by means of a Haake viscometer, of from 1000 to 3000 mPa·s and are therefore  
40 readily processible, while analogous polyisocyanate compositions having the same urethane group content/kg, but modified, for example, by means of dipropylene glycol, are already solid.

45 The polyisocyanate compositions according to the invention having a urethane group content of from 0.1 to 2 mol/kg usually have a content of NCO groups of from 18 to 30% by



weight, preferably from 24 to 28% by weight, based on the total weight.

- 5 The novel crude MDI compositions containing urethane groups can be used for the preparation of any, preferably highly crosslinked polyisocyanate polyaddition products. They have proven particularly successful and are therefore preferred for the preparation of polyisocyanate polyaddition products for whose preparation relatively highly functional polyisocyanates, for example those having a functionality of at least 2.5, must be mixed with polyhydroxyl components (A) containing polyoxyalkylene-polyols having a functionality of at least 3 and a hydroxyl number of at least 250, preferably at least 350. Polyisocyanate polyaddition products of this type are in particular crosslinked PU elastomers and rigid PU (molded) foams.
- 10
- 15
- c) 20 The compact or cellular polyurethanes can be prepared by the novel process in the presence or absence of chain extenders and crosslinking agents (c). In the preparation of flexible, compact or cellular polyurethanes, the addition of chain extenders, crosslinking agents or, if desired, mixtures thereof may prove advantageous for modification of the mechanical properties, for example the hardness. In the production of rigid PU foams, the use of chain extenders and/or crosslinking agents (c) is usually unnecessary. Chain extenders which can be used are difunctional compounds, and crosslinking agents which can be used are trifunctional and higher functional compounds, in each case having a molecular weight of less than 400, preferably from 62 to approximately 300. Specific examples of chain extenders which may be mentioned are alkanediols, for example those having 2 to 6 carbon atoms in the alkylene radical, eg. ethanediol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol and 1,6-hexanediol, and dialkylene glycols, eg. diethylene glycol, dipropylene glycol and dibutylene glycol, and specific examples of crosslinking agents which can be used are alkanolamines, eg. ethanolamine, dialkanolamines, eg. diethanolamine, and trialkanolamines, eg. triethanolamine and triisopropanolamine, trihydric and polyhydric alcohols, eg. glycerol, trimethylolpropane and pentaerythritol, and aliphatic and/or aromatic diamines, eg. 1,2-ethanediamine, 1,4-butanediamine, 1,6-hexanediamine, 2,3-, 2,4- and/or 2,6-tolylenediamine, 4,4'-diaminodiphenylmethane, 3,5-di thyl-2,4- and/or 2,6-tolylenediamine, 3,3'-di- and/or 3,3',5,5'-t traalkyl-3,3-diaminodiphenylmethanes, eg. tetraisopropyl-4,4'-diaminodiphenylmethane. Other suitable chain xtenders or crosslinking agents are
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low-molecular-weight ethoxylation and/or propoxylation products, eg. those having molecular weights of up to approximately 400, of the abovementioned polyhydric alcohols, alkylene glycols, alkanolamines and diamines.

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Preferred chain extenders are alkanediols, in particular 1,4-butanediol and/or 1,6-hexanediol, alkylene glycols, in particular ethylene glycol and propylene glycol, and preferred crosslinking agents are trihydric alcohols, in particular glycerol and trimethylolpropane, dialkanolamines, in particular diethanolamine, and trialkanolamines, in particular triethanolamine.

15

The chain extenders and/or crosslinking agents preferably used for the preparation of flexible, compact or cellular polyurethanes can be employed, for example, in amounts of from 2 to 60% by weight, preferably from 10 to 40% by weight, based on the total weight of formative components (a) and (c).

20

d) The blowing agent (d) for the preparation of the cellular polyurethanes, preferably rigid PU foams, is, in particular, water, which reacts with isocyanate groups to form carbon dioxide. The amounts of water expediently employed are from 0.1 to 8 parts by weight, preferably from 1 to 5 parts by weight, in particular from 1.5 to 3 parts by weight, based on 100 parts by weight of the polyhydroxyl compounds (a).

30

Other suitable blowing agents are liquids which are inert toward the liquid polyisocyanate compositions (b) modified by means of urethane groups and which have boiling points of below 100°C, preferably below 50°C, in particular from -50°C to 30°C, at atmospheric pressure, so that they evaporate under the conditions of the exothermic polyaddition reaction, and mixtures of these physical blowing agents and water.

35

Examples of preferred liquids of this type are alkanes, eg. heptane, hexane, n- and isopentane, preferably technically-grade mixtures of n- and isopentanes, n- and isobutane and propane, cycloalkanes, such as cyclopentane and/or cyclohexane, ethers, eg. furan, dimethyl ether and diethyl ether, ketones, eg. acetone and methyl ethyl ketone, alkyl

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carboxylates, such as methyl formate, dimethyl oxalate and ethyl acetate, and halogenated hydrocarbons, such as methylene chloride, dichloromonofluoromethane, difluoromethane, trifluoromethane, difluoroethane, tetrafluoroethane, chlorodifluoroethanes, 1,1-dichloro-2,2,2-trifluoroethane, 2,2-dichloro-2-fluoroethane and heptafluoropropane. It is also

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possible to use mixtures of these low-boiling liquids with one another and/or with other substituted or unsubstituted hydrocarbons. Also suitable are organic carboxylic acids, eg. formic acid, acetic acid, oxalic acid, ricinoleic acid and carboxyl-containing compounds.

Other blowing agents (d) which can be used are compounds which are pulverulent at room temperature and which decompose at elevated temperature through elimination of gases, eg. steam, carbon dioxide, carbon monoxide, oxygen or nitrogen. Specific examples which may be mentioned are silica gels, bicarbonates, ammonium formate, oxalic acid derivatives, urea and urea derivatives, peroxides and preferably azo compounds, eg. azoisobutyronitrile and azodicarbonamide, hydrazines, eg. 4,4'-oxybis(benzenesulfohydrazide) and diphenyl sulfone 3,3'-disulfohydrazide, semicarbazides, eg. p-toluenesulfonylsemicarbazide, and triazoles, eg. 5-morpholyl-1,2,3,4-thiatriazole.

Preferred blowing agents are chlorodifluoromethane, chlorodifluoroethanes, dichlorofluoroethanes, pentane mixtures, cyclopentane, cyclohexane and in particular water, and mixtures of at least two of these blowing agents, eg. mixtures of water and cyclopentane, mixtures of chlorodifluoromethane and 1-chloro-2,2-difluoroethane and, if desired, water. Chlorofluorocarbons, which damage the ozone layer, are not used as blowing agents.

The requisite amount of physical blowing agents can readily be determined experimentally depending on the foam density required and any water employed and is from about 0 to 25 parts by weight, preferably from 0 to 15 parts by weight, per 100 parts by weight of the polyhydroxyl compounds (a). It may be expedient to mix the polyisocyanate composition (b) containing bonded urethane groups with the inert physical blowing agent and thus to reduce its viscosity.

e) If the compact or cellular polyurethanes are prepared in the presence of catalysts, preferred compounds for this purpose are those which greatly accelerate the reaction of the hydroxyl-containing compounds of formative component (a) and, if used, (c) with the liquid, MDI-based polyisocyanate compositions (b) containing bonded urethane groups. Suitable compounds are organotin compounds, preferably organotin compounds, such as tin(II) salts of organic carboxylic acids, eg. tin(II) acetate, tin(II) octanoate, tin(II) ethylhexanoate and tin(II) laurate, and the dialkyltin(IV) salts of

organic carboxylic acids, eg. dibutyltin diacetate, dibutyltin dilaurate, dibutyltin maleate and dioctyltin diacetate, and highly basic amines, for example amidines, eg. 2,3-dimethyl-3,4,5,6-tetrahydropyrimidine, tertiary amines, eg. triethylamine, tributylamine, dimethylbenzylamine, N-methyl-, N-ethyl- and N-cyclohexylmorpholine, N,N,N',N'-tetramethylethylenediamine, N,N,N',N'-tetramethylbutanediamine, N,N,N',N'-tetramethyl-1,6-hexanediamine, di(4-dimethylaminocyclohexyl)methane, pentamethyldiethylenetriamine, tetramethyldiaminoethyl ether, bis(dimethylaminopropyl)urea, dimethylpiperazine, 1,2-dimethylimidazole, 1-azabicyclo[3.3.0]octane and preferably 1,4-diazabicyclo[2.2.2]octane, and alkanolamine compounds, such as triethanolamine, triisopropanolamine, N-methyl- and N-ethyldiethanolamine and dimethylethanolamine.

Other suitable catalysts are: tris(dialkylaminoalkyl)-s-hexahydrotriazines, in particular tris(N,N-dimethylaminopropyl)-s-hexahydrotriazine, tetraalkylammonium hydroxides, such as tetramethylammonium hydroxide, alkali metal hydroxides, such as sodium hydroxide, and alkali metal alkoxides, such as sodium methoxide, sodium ethoxide, potassium ethoxide and potassium isopropoxide, and alkali metal salts of long-chain fatty acids having 10 to 20 carbon atoms and possibly pendant OH groups, and combinations of the organometallic compounds and highly basic amines. It is preferred to use from 0.001 to 5% by weight, in particular from 0.05 to 2% by weight, of catalyst or catalyst combination, based on the weight of the polyhydroxyl compound (a).

f) Auxiliaries (f) can, if desired, also be incorporated into the reaction mixture for the preparation of the compact and cellular polyurethanes. Examples which may be mentioned are surfactants, foam stabilizers, cell regulators, fillers, dyes, pigments, flameproofing agents, antihydrolysis agents and fungistatic and bacteriostatic substances.

Examples of suitable surfactants are compounds which serve to support homogenization of the starting materials and may also regulate the cell structure. Specific examples are emulsifiers, such as the sodium salts of castor oil sulfates, or of fatty acids, and the salts of fatty acids with amines, for example diethylamine oleate, diethanolamine stearate and diethanolamine ricinoleate, salts of sulfonic acids, eg. alkali metal salts or ammonium salts of dodecylbenzene- or dinaphthylmethanedisulfonic acid and ricinoleic acid; foam stabilizers, such as siloxane-oxyalkylene copolymers and

other organopolysiloxanes, oxy thylated alkylphenols, oxy-thylated fatty alcohols, paraffin oils, castor oil esters, ricinoleic acid esters, Turkey red oil and groundnut oil, and cell regulators, such as paraffins, fatty alcohols and dimethylpolysiloxanes. Suitable compounds for improving the emulsification action, the cell structure and/or stabilizing the foam are furthermore oligomeric polyacrylates containing polyoxyalkylene and fluoroalkane radicals as side groups. The surfactants are usually used in amounts of from 0.01 to 5 parts by weight, based on 100 parts by weight of the polyhydroxyl compounds (a).

For the purposes of the present invention, fillers, in particular reinforcing fillers, are conventional organic and inorganic fillers and reinforcing agents. Specific examples are inorganic fillers, such as silicate minerals, for example phyllosilicates, such as antigorite, serpentine, hornblendes, amphiboles, chrysotile, talc; metal oxides, such as kaolin, aluminum oxides, aluminum silicate, titanium oxides and iron oxides, metal salts, such as chalk, barytes and inorganic pigments, such as cadmium sulfide, zinc sulfide and glass particles. Examples of suitable organic fillers are carbon black, melamine, colophony, cyclopentadienyl resins and graft polymers.

The inorganic and organic fillers may be used individually or as mixtures and are advantageously introduced into the reaction mixture in amounts of from 0.5 to 50% by weight, preferably from 1 to 40% by weight, based on the weight of components (a) to (c).

Examples of suitable flameproofing agents are tricresyl phosphate, tris(2-chloroethyl) phosphate, tris(2-chloropropyl) phosphate, tris(1,3-dichloropropyl) phosphate, tris(2,3-dibromopropyl) phosphate and tetrakis(2-chloroethyl)ethylene diphosphate.

In addition to the abovementioned halogen-substituted phosphates, it is also possible to use inorganic flameproofing agents, such as red phosphorus, aluminum oxide hydrate, antimony trioxide, arsenic oxide, ammonium polyphosphate, expandable graphite and calcium sulfate, or cyanuric acid derivatives, eg. melamine, or mixtures of two or more flameproofing agents, eg. ammonium polyphosphates and melamine and/or expandable graphite and, if desired, starch, in order to flameproof the compact or cellular polyurethanes prepared according to the invention. In general, it has proven expedient

to use from 5 to 50 parts by weight, preferably from 5 to 25 parts by weight, of said flameproofing agents or mixtures per 100 parts by weight of components (a) to (c).

- 5 Further details on the other conventional auxiliaries mentioned above can be obtained from the specialist literature, for example from the monograph by J.H. Saunders and K.C Frisch, High Polymers, Volume XVI, Polyurethanes, Parts 1 and 2, Interscience Publishers 1962 and 1964 respectively, or
- 10 Kunststoff-Handbuch, Polyurethane, Volume VII, Carl-Hanser-Verlag, Munich, Vienna, 1st and 2nd Editions, 1966 and 1983.

In order to prepare the compact or cellular polyurethanes, the liquid polyisocyanate compositions (b) containing bonded urethane

15 groups, the relatively high-molecular-weight polyhydroxyl compounds (a) and, if desired, chain extenders and/or crosslinking agents (c) can be reacted in the absence or preferably presence of catalysts (e) and auxiliaries (f) and in the presence of blowing agents (d) for the formation of cellular polyurethanes at

20 from 0 to 100°C, preferably from 15 to 80°C, in such mixing ratios that from 0.5 to 2, preferably from 0.8 to 1.3, in particular approximately one, reactive hydrogen atom(s) bonded to formative component (a) and, if used, (c) are present per NCO group and, if water is used as blowing agent, the molar ratio between the num-

25 ber of equivalents of water and the number of equivalents of NCO groups is from 0.5 to 5 : 1, preferably from 0.7 to 0.95 : 1, in particular from 0.75 to 0.85 : 1.

The compact and cellular polyurethanes can be prepared by the

30 prepolymer process or preferably by the one-shot process by mixing two components (A) and (B), where formative components (a) and, if used, (c), (d), (e) and (f) are combined to form the polyhydroxyl component (A) and the polyisocyanate component (B) comprises the diphenylmethane diisocyanate-based polyisocyanate

35 composition (b) containing bonded urethane groups, if desired mixed with (f) and inert, physical blowing agents. Since the polyol component (A) and the polyisocyanate component (B) have very good shelf lives, they need only be mixed intensively before preparation of the compact or cellular polyurethanes. The reac-

40 tion mixture can be brought to reaction in open or closed molds, expediently at from 15 to 80°C.

In order to prepare cellular polyurethanes, eg. flexible, semi-rigid or preferably rigid polyurethane foams, preferably PU

45 molded foams, the foamable reaction mixture can be introduced into an expediently metallic, temperature-controllable, open or closed mold at, for example, from 15 to 80°C, preferably at from

18 to 45°C. The mold temperature is usually from 20 to 90°C, preferably from 35 to 70°C. The reaction mixture is allowed to cure in the closed mold, usually with compaction, for example with degrees of compaction of from 1.1 to 8, preferably from 2 to 6, 5 in particular from 2.5 to 4. The novel process is also suitable for the production of polyurethane slabstock foams.

The compact polyurethanes generally have densities of from 1.0 to 1.2 g/cm<sup>3</sup>, products of higher density being obtained with addition 10 of reinforcing materials and/or fillers. Cellular elastomers and PU structural foams usually have densities of from 240 to less than 1000 g/l, densities of from 400 to 600 g/l being preferred. The flexible, semirigid and preferably rigid PU foams expediently have densities of from 30 to 80 g/l, preferably from 35 to 15 60 g/l.

The compact polyurethanes prepared by the novel process are used, for example, in the automotive, construction and furniture industries, for example as rain gutters, side strips, cover panels and 20 table edges; the cellular PU elastomers are used, for example, as damping elements, sun visors, armrests, shoe inners and shoe soles; and the PU foams are used, for example, as cushioning materials, safety covers, furniture housings, for foam-filling refrigeration equipment housings, for example chest freezers and 25 refrigerators, hot-water equipment, district heating pipes and cavities of all types, and for rock consolidation.

#### Examples

30 Preparation of the liquid polyisocyanate compositions containing urethane groups

#### Example 1

35 0.1 part by weight of benzoyl chloride was added with stirring to 4000 parts by weight of crude MDI having an NCO content of 31% by weight and a content of MDI isomers of 40% by weight under a nitrogen atmosphere in a reactor fitted with stirrer, reflux condenser and feed and withdrawal device for gases, the reaction 40 mixture was warmed to 50°C, and 211 parts by weight of isopropanol were added dropwise at this temperature over a period of 30 minutes, during which the reaction temperature rose to 70°C. The reaction mixture was then warmed to 80°C and the reaction was completed at this temperature in 2 hours, giving a clear, flowable 45 polyisocyanate composition having a urethane group content of 0.84 mol/kg, and an NCO content of 25.9% by weight and a

viscosity at 23°C of 2100 mPa·s, measured using a Haake viscometer (Rotovisko RV 20 type).

By varying the amount of isopropanol, polyisocyanate compositions having different concentrations of urethane groups were prepared analogously.

The amount of isopropanol used, the percentage contents of urethane and isocyanate groups and the viscosity of the polyisocyanate compositions and their miscibility with trioxypropylene glycol are shown in Table 1.

Examples 2 and 3

The procedure was similar to that of Example 1, but the isopropanol was replaced as monohydric alcohols by methanol and allyl alcohol in the amounts shown below.

Comparative Example I

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The procedure was similar to that of Example 1, but the isopropanol was replaced by difunctional dipropylene glycol.

Miscibility with polyoxyalkylene-polyols

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In order to test the miscibility, equimolar amounts of the crude MDI compositions containing urethane groups and trioxypropylene glycol (TPG) were mixed at 23°C.

The test substance used in place of polyoxyalkylene-polyols was trioxypropylene glycol, since this compound has a similar hydroxyl number to rigid foam polyoxyalkylene-polyols, but has low viscosity and is therefore more suitable for mixing trials of this type than, for example, sucrose-based polyoxyalkylene-polyols, which have high viscosity.

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Tabl 1  
Physical properties of the polyisocyanate compositions containing urethane groups

Ex- ample	Alcohol Type	Amount [parts by weight]	Urethane group content [mol/kg]	NCO content [% by weight]	Viscosity [mPa·s]	Miscibility with TPG [equimolar]
1	Isopropanol	120	0.49	28.1	1000	fine emulsion
	"	140	0.56	27.6	1400	"
	"	160	0.64	27.1	1610	miscible giving a clear mixture
	"	200	0.79	26.0	1990	"
	"	211	0.84	25.9	2100	"
	"	240	0.94	25.3	3120	"
	"	360	1.38	22.7	4800	"
2	Methanol	80	0.61	27.8	1320	fine emulsion
	"	100	0.76	27.0	1980	miscible giving a clear mixture
	"	120	0.91	26.3	3000	"
	"	160	1.20	24.8	4830	"
3	Allyl alcohol	132	0.55	27.7	1350	miscible giving a clear mixture
Comp. Ex. I	Dipropylene glycol	60	0.22	30.0	3050	immiscible
	"	80	0.29	29.7	6800	"
	"	100	0.36	29.4	18640	"

## Preparation of cellular polyurethanes

## Example 4

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## Rigid PU foam

Polyhydroxyl component (A): a mixture comprising

- 10 93 parts by wt. of trioxypylene glycol (hydroxyl  
number 584),  
2.4 parts by wt. of polysiloxane foam stabilizer  
(Tegostab®B8406 from Goldschmidt AG),  
1.9 parts by wt. of dimethylcyclohexylamine and  
15 2.7 parts by wt. of water.

Polyisocyanate component (B):

- Crude MDI composition having a urethane group content of  
20 0.79 mol/kg, an NCO content of 26% by weight and a viscosity at  
23°C of 1990 mPas, measured using a Haake viscometer,  
Rotovisko RV 20 type, prepared as described under Example 1 by  
reacting 200 parts by weight of isopropanol with 4000 parts by  
weight of the crude MDI described in Example 1.

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- In order to prepare the rigid PU foam, 100 parts by weight of the  
polyhydroxyl component (A) and 229 parts by weight of the  
polyisocyanate component (B) were mixed vigorously at 23°C, and  
the clear reaction mixture was transferred into a plastic bucket,  
30 where it was allowed to expand.

## Comparative Example II

Polyhydroxyl component (A): as in Example 4

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Polyisocyanate component (B): crude MDI having an NCO content of  
31% by weight and an MDI isomer content of 40% by weight.

- 100 parts by weight of the polyhydroxyl component (A) and  
40 188 parts by weight of the polyisocyanate component (B) were  
mixed and allowed to expand as described in Example 4.

Table 2

Mechanical properties of the rigid PU foams, prepared as  
5 described in Example 4 and Comparative Example II

	Mechanical properties	Ex. 4	Comp. Ex. II
	Density [g/l]	52.5	47.1
10	Thermal conductivity, [mW/mK] measured using a Hesto lambda control A 50-A	20.1	21.5
	Proportion of closed cells, [%] measured using a Beckmann air comparative pycnometer, Model 930	87	88
15	Compressive strength in accordance with DIN 53421 [kPa]	494	306
20	Maximum reaction temperature [°C] in the foam core, measured using a Cr-Ni thermocouple with a thickness of 0.2 mm	181	206

## Example 5

## Rigid PU foam

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Polyhydroxyl component (A): a mixture comprising

- 81.6 parts by wt. of a glycerol-initiated polyoxypropylene-polyol  
having a hydroxyl number of 400,  
30 9.9 parts by wt. of trioxypropylene glycol,  
2.5 parts by wt. of polysiloxane foam stabilizer  
(Polyurax® SR 321 from Union Carbide),  
2.0 parts by wt. of dimethylcyclohexylamine and  
3.0 parts by wt. of water.

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Polyisocyanate component (B): as in Example 4

- In order to prepare the rigid PU foam, 100 parts by weight of the  
polyhydroxyl component (A) and 179 parts by weight of the  
40 polyisocyanate component (B) were mixed as in Example 4 and  
allowed to expand freely.

## Comparative Example III

- 45 Polyhydroxyl component (A): as in Example 5

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Polyisocyanate component (B): as in Comparativ Examl II

100 parts by weight of the polyhydroxyl component (A) and  
152 parts by weight of the polyisocyanate component (B) were  
5 mixed and allowed to expand as in Example 4.

Table 3

Mechanical properties of the rigid PU foams, prepared as  
10 described in Example 5 and Comparative Example III

Mechanical properties		Ex. 5	Comp. Ex. III
15	Density [g/l]	44.6	40.8
	Thermal conductivity, [mW/mK] measured using a Hesto lambda control A 50-A	20.9	22.1
20	Proportion of closed cells, [%] measured using a Beckmann air comparative pycnometer, Model 930	89	89
	Compressive strength in accordance with DIN 53421 [kPa]	368	287

25 Example 6

Compact PU molding composition

100 parts by wt. of a polyoxypropylene glycol having a hydroxyl  
number of 105 prepared by polyaddition of  
30 1,2-propylene oxide onto 1,2-propanediol

were dried for 2 hours at 100°C under reduced pressure (about  
35 10 mbar) and then mixed with

0,1 part by wt. of dibutyltin dilaurate.

33 parts by wt. of the flowable, crude MDI/isopropanol-based  
polyisocyanate composition described in  
40 Example 1, having an NCO content of 25.9%  
by weight,

were added at 23°C with vigorous stirring using a propeller  
45 stirrer.

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The reaction mixture was transferred into a metallic mold having the internal dimensions 20x10x0.5 cm which was held at a temperature of 50°C, and allowed to react there, and the PU elastomer formed was demolded after one hour.

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A clear, bubble-free, dark-brown PU sheet was obtained on which the following mechanical properties were measured:

Tear strength	[N/mm <sup>2</sup> ]:	0.92
10 Elongation at break	[%]:	102

#### Comparative Example IV

The procedure was similar to that described in Example 6, but the flowable crude MDI/isopropanol-based polyisocyanate composition was replaced by unmodified crude MDI having an NCO content of 31% by weight.

An inhomogeneous, yellow-brown PU sheet containing numerous gas bubbles was obtained on which the following mechanical properties were measured:

Tear strength	[N/mm <sup>2</sup> ]:	0.26
Elongation at break	[%]:	44

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We claim:

1. A process for the preparation of compact or cellular polyurethanes by reacting
  - a) relatively high-molecular-weight polyhydroxyl compounds containing at least two reactive hydrogen atoms with
  - b) liquid, diphenylmethane diisocyanate-based polyisocyanate compositions containing bonded urethane groups,in the presence or absence of
  - c) chain extenders and/or crosslinking agents,
  - d) blowing agents,
  - e) catalysts and
  - f) auxiliaries,wherein the polyisocyanate compositions (b) used are obtainable by reacting mixtures of diphenylmethane diisocyanates and polyphenylpolymethylene polyisocyanates with a substoichiometric amount of at least one linear, branched or cyclic, saturated or olefinically unsaturated, low-molecular-weight monoalcohol.
2. A process as claimed in claim 1, wherein the relatively high-molecular-weight polyhydroxyl compounds (a) have a functionality of from 2 to 8 and a molecular weight of from 400 to 8000, and the chain extenders and/or crosslinking agents (c) have a functionality of from 2 to 5 and a molecular weight of less than 400.
3. A process as claimed in claim 1, wherein the mixture of diphenylmethane diisocyanates and polyphenylpolymethylene polyisocyanates which can be used for the preparation of the polyisocyanate compositions (b) has a diphenylmethane diisocyanate isomer content of from 30 to 95% by weight.
4. A process as claimed in claim 1, wherein the low-molecular-weight alcohols which can be used for the preparation of the polyisocyanate compositions (b) have 1 to 6 carbon atoms.

5. A process as claimed in claim 1, wherein 1 kg of polyisocyanate composition contains from 0.1 to 2 mol of urethane groups.
- 5 6. A liquid polyisocyanate composition containing urethane groups, obtainable by reacting a mixture of diphenylmethane diisocyanates and polyphenylpolymethylene polyisocyanates with a substoichiometric amount of at least one linear, branched or cyclic, saturated or olefinically unsaturated  
10 monoalcohol having 1 to 6 carbon atoms.
7. A liquid polyisocyanate composition containing urethane groups as claimed in claim 6, which is prepared using a mixture of diphenylmethane diisocyanates and polyphenylpolymethylene polyisocyanates containing from 30 to 95% by weight  
15 of diphenylmethane diisocyanate isomers.
8. A liquid polyisocyanate composition containing urethane groups as claimed in claim 6, which contains from 0.1 to  
20 2 mol of urethane groups per kg.
9. A liquid polyisocyanate composition containing urethane groups as claimed in claim 6, wherein the monoalcohols used are methanol, ethanol, n-propanol, isopropanol and/or allyl  
25 alcohol.
10. The use of a liquid polyisocyanate composition containing urethane groups as claimed in claim 6 for the production of rigid polyurethane foams.  
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